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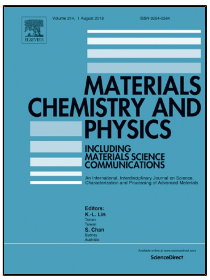


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# Activated nanocarbons produced by microwave-assisted hydrothermal carbonization of Amazonian fruit waste for methane storage

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**Abstract**

This work reports the preparation and characterization of biomass-derived renewable microporous carbon nanoparticles obtained by microwave-assisted hydrothermal carbonization (MAHC), following by physical activation, of assai stone waste. Conventional routes (i.e. carbonization in furnace and chemical activation) was also investigated. The highest yield provided by MAHC combined with $CO_2$ as activating agent resulted in nanocarbons with surface area of 1100 $m^2/g$ and a very narrow pore size distribution with a micropore volume of 0.45 $cm^3/g$. Owing to the excellent combination of microporosity and high bulk density (0.89 $g/cm^3$). The biomass-derived carbon shows great potential to be used as adsorbent for natural gas storage. Indeed, high pressure methane adsorption isotherm in volumetric basis revealed an uptake value of 140 V(STP)/V at 25 °C and 4 MPa.

**Keywords:** Carbon nanoparticles; biomass, hydrothermal microwave carbonization, methane storage.

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## 1. Introduction

Natural gas is a clean, safe and abundant energy source. Gas storage and transportation have advantages that attract global attention [1]. The use of natural gas for various industrial and domestic sectors is limited by the lack of a gas distribution network (pipeline and storage vessel) and the long distance of the point of use and source of supply. Adsorbed natural gas (ANG) is a safer alternative to the compressed natural gas technology that could offer a solution for the distribution of natural gas in remote location. Despite this technology has being investigated for a long time it is still not competitive in the market since the synthesis of the adsorbent materials suitable for this application has to be available in tons and, at the same time, its synthesis must fulfill ecological and economical demands [2]. Additionally, current studies on adsorbed natural gas (ANG) are guided by targets set by energy companies and governmental sectors. The most commonly found on literature is the target of 180 $cm^3$ (STP) at 3.5 MPa set by the United States Department of Energy (DOE) [3], as the stored gas volume that must be delivered from an ANG system for it to be considered economically feasible. More recently set at 263 $cm^3$ (STP) at room temperature and.6.5 MPa (ARPA-E 2012). This new ambitious value was only reached by a metal organic framework, HKUST-1, prepared recently in monolith form exhibiting a density of 1.06 $g.cm^{-3}$ (Tian et al. 2017) and a $CH_4$ uptake of 259 V/V.

Activated carbons (ACs) with microporous structures constitute an important category of potential adsorbents for natural gas storage [6] . Properties of activated carbon required for natural gas adsorption includes: high micropores volume, high packing density, high adsorption desorption rate, high working capacity (difference between the maximal adsorption pressure to 0.1 MPa) [7], less susceptible to temperatures changes during adsorption and desorption and chemical stability [8].

The election of abundant and cheap carbon precursors is crucial to the final cost of the activated carbon as well as it is the election of a green and facile synthesis method to make the whole process scalable. In this regard, the Amazon forest is one of the largest biomass reservoirs in the world, and recently, assai fruit (*Euterpe oleracea*), an agrosilvicultural product part of the traditional diet of the local population at the river Delta of the Amazon is gaining local national and even international market [9]. In 2013 the Brazilian Amazonian region produced approximately 183,000 tons of assai (fruit). These numbers are translated in the quantities of stone and pulp produced as waste, which represent almost the 85 % of the fruit, thus, making assai waste very attractive to be used as a massive lignocellulosic carbon precursor to produce microporous activated carbons.

Beyond the several ACs producing methods, direct combustion processes, thermochemical processes, biochemical processes, which include pyrolysis, gasification and liquefaction [10], the microwave-assisted hydrothermal carbonization (MAHC) [11] can be a promising low-cost and facile synthesis method for producing ACs from assai waste. Microwave irradiation offers homogenous and fast heating process that significantly reduces time and cost in the synthesis comparing to the conventional processes at high temperatures [12]. On the other hand, hydrothermal carbonization is a method originally developed by Titirici et al [13] that consists on the conversion of pure carbohydrates as well as lignocellulosic biomass into a valuable carbon material using mild processing temperatures (<200 ºC) and water as a carbonization medium, under self-generated pressures. This method, in principle can improve considerable the bio-char yield. Assai stone is composed 68.75 % of cellulose, making it ideal for the hydrothermal carbonization.

Therefore, this work reports the preparation and characterization of biomass-derived renewable microporous carbon material using assai stone as starting material processed

by Microwave-Assisted Hydrothermal Carbonization (MAHC). A comparison with other conventional synthesis routes will be also discussed. Finally, the material will be evaluated for methane storage.

## 2. Experimental

### *2.1. Thermogravimetric Analysis*

The thermal degradation of assai stone under inert and oxidizing atmosphere was carried out in a METTLER TOLEDO model TGA/SDTA851and/SF/1100 TG-DTA using $N_2$, $CO_2$ and air as carrier gas (50 $cm^3$/min) with a heating rate of 10 °C/ min up to 1000 °C.

### *2.2. Elemental Analysis*

An elemental analyser (Thermo Finnigan Flash 1112) was used to determine the weight percentages of carbon, hidrogen and nitrogen.

### *2.3. Microwave-assisted hydrothermal carbonization (MAHC) and conventional carbonization*

Assai stones were used as-received as raw material. The stones were washed with water prior to experiments. Aqueous suspensions of the raw material were prepared using citric acid (Merck) as catalyst reagent. A 1.5 mol/L catalyst stock solution was prepared in Milli-Q water. Approximately 500 mg of shells (a total of 8 samples) were poured in a reaction container filled with 10 mL of stock solution. The suspensions were placed in a 100 mL PTFE sealed reactor for microwave processing. The materials were hydrothermally carbonized using a microwave labstation (CEM MARS, USA) operating at 2.45 GHz, with 1600 W maximum power and 10 W pulse controlled power fractions. The system was heated from 20 °C to 85 °C at 22 °C/min, then from 85 °C to 145 °C at

7 °C/min, and from 145 °C to 200 °C at 14 °C/min. Finally, an isotherm was held at 200 °C for 120 min. The samples were labeled Assai MW.

For conventional carbonization (CC) 10 g of raw material were placed in a tubular oven at 500 ºC for 2 hours under $N_2$ atmosphere with flow of 80 ml/min and a heating rate of 10 °C/min. The samples were labeled as Assai CC.

*2.4. Physical and chemical activations*

The carbonized samples (MAHC and CC) were activated in a tubular furnace under a flow of 80 mL $CO_2$/min at 880 ºC for 5 h. The samples were labeled as Assai MW $CO_2$ and Assai CC $CO_2$. For chemical activation, a physical mixture of KOH and assai conventionally carbonized samples (approximately 500 mg) with KOH:precursor ratio of 2:1 has been prepared. Activation treatment was carried out in a horizontal furnace at 600 ºC for 2 h, under a nitrogen flow of 100 ml/min, using a heating rate of 10 ºC/min. The final materials were washed with 10 %HCl solution and with distilled water, until complete removal of chloride ions, and finally, dried overnight. The sample was labeled as Assai CC KOH.

*2.5. Textural characterization*

The textural properties of the synthesized ACs were analyzed using nitrogen adsorption at -196 °C and carbon dioxide at 0 °C. Gas adsorption measurements were performed in an automated manometric equipment (N2Gsorb-6, Gas to Materials Technologies). All samples were previously degassed under vacuum ($10^{-4}$ MPa) for 4 h at 250 °C. $N_2$ adsorption data were used to determine the total pore volume ($V_t$) at a relative pressure ($P/P_0$) around 0.95, the specific surface area (after application of the B.E.T. equation), and the total micropore volume ($V_0$), through the Dubinin–Radushkevich equation (DR)

(Wegrzyn and Gurevich 1996; Nguyen and Do 2001). The difference between the $V_t$ and $V_0$ was considered the volume of mesopores ($V_{meso}$). $CO_2$ adsorption data at 0 °C were used to determine the narrow micropore volume ($V_n$), after application of the DR equation. Pore size distribution was calculated by applying the Non-Local Density Functional Theory (NLDFT) to $CO_2$ adsorption data for pores below 1 nm.

*2.6. High pressure measurements*

The $CH_4$ adsorption capacity was measured at 25 °C and up to a final pressure of 4.5 MPa. Before any adsorption experiment, samples were degassed at 250 °C for 4 h. High-pressure analyses were performed in a home-made fully automated manometric equipment designed and constructed by the Advanced Materials group (LMA), now commercialized as iSorbHP by Quantachrome Instruments.

*2.7 Determination of packing density and helium density*

Packing density has been determined by pressing a given mass of activated carbon in a mold with a cross-sectional area of 1.30 $cm^2$ at pressure of 753 $kg/cm^2$. Helium density, which represents the skeleton density of carbon ($\rho_{He}$), was measured in a helium pycnometer (Model Accupyc 1330). Samples were dried in the oven overnight before measurements.

## 3. Results and discussion

*3.1 Thermal behavior of the assai stones*

The first step in the production of activated carbon from biomass is the thermochemical conversion of the raw material into a bio-char under inert atmosphere. Then, thermogravimetric (TG) analysis results can anticipate the possible yield if a conventional

carbonization under $N_2$ is carried out. Likewise, TGAs in air and $CO_2$, provide information for the proper election of the activation conditions, which is the second step in the development of porous carbons.

To know more about the thermal stability of the assai stone, Fig. 1 shows the evolution of the mass during heating under $N_2$, $CO_2$ and air.

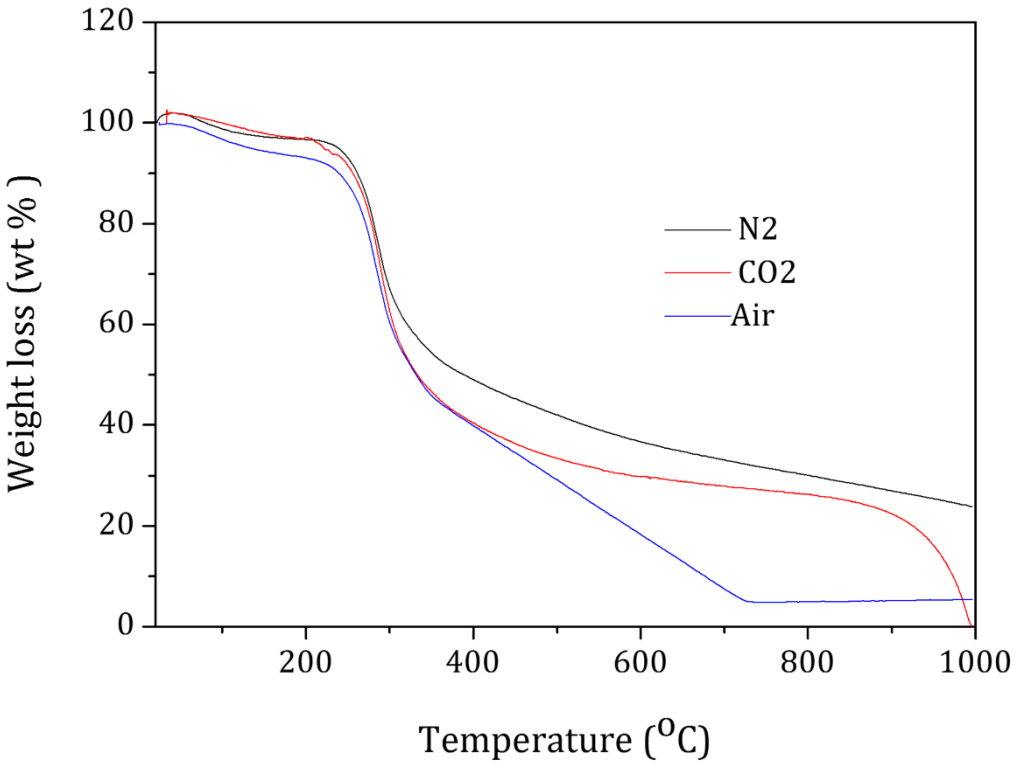


**Fig 1**. Thermogravimetric analysis (TG) curves of assai stone under three different atmospheres, $N_2$, $CO_2$ and air.

The first stage of the TG curves (until 200 ºC), corresponds to water release [16]. In general, the thermal stability of the raw material is very low, even under inert atmosphere, as confirmed by a sharp weight loss in common for the three gases between 230ºC and 350 ºC, which can be attributed to the cellulose decomposition [17]. In this step, around 60% of the sample is decomposed, which is in agreement with the cellulose content of the assai stone (68.75% calculated by Van Soest technique) [18]. In the case of the inert

atmosphere, $N_2$, the weight loss continues diminishing progressively until it reaches 25% of the initial mass at 1000 ºC, which corresponds to bio-char formation. Under $CO_2$, the mass reaches 20% at 900 ºC. Afterwards, an abrupt decay occurs with the completely disappearance of the product (in air the weight decays until zero even at the lower temperature of 700 ºC). This second weight loss under the three atmospheres can be attributed to the decomposition of lignin (assai stone comprises14.05 % of lignin).

*3.2 Microwave-assisted hydrothermal carbonization and conventional carbonization*

The assai stone was submitted to a conventional carbonization at 500 ºC under $N_2$ following by physical activation at 880 ºC under $CO_2$ (Assai CC $CO_2$). According to TGA results, at these temperatures the biopolymers are decomposed. The chemical activation with KOH at 800 ºC was also tested (Assai CC KOH). The carbonization yield can be seen in Table 2. The value of 24% agrees with TG results. The chemical activation with KOH resulted in a yield of 42% using the ratio 2:1 (KOH:bio-char, wt.%:wt.%).

Conversely, during the physical activation sample was consumed. To solve this drawback, microwave-assisted hydrothermal carbonization (MAHC) seems to be a suitable alternative solution.

The hydrothermal carbonization is consisting on the conversion of pure carbohydrates as well as lignocellulosic biomass into a valuable carbon materials using mild processing temperatures (<200 ºC) and water as a carbonization medium, under self-generated pressures. This method, in principle can improve considerable the bio-char yield. Assai stone contents 68.75 % of cellulose, making it ideal for the hydrothermal carbonization. Combined with microwave irradiation, which offers a fast and homogenous heating process, the assai stone was converted into carbon with high yield, 63.5 %, much higher than the conventional carbonization in a furnace at high temperature

(Table 2). The elemental analysis shown in Table 1 confirms the enhancement in the carbon content from 41.45 wt.% for the raw material to 63.17 wt.% after the MAHC process.

Table 1 show the composition of the assai stone that was used as raw material

| Sample | N (wt.%) | C (wt.%) | H (wt.%) | O*(wt.%) |
|---|---|---|---|---|
| **Assai stone** | 0.72 | 41.45 | 6.32 | 51.51 |
| **Assai stone MW** | 0.28 | 63.17 | 4.3 | 32.25 |

*O% was determined by difference.

Figure 2 shows SEM images of the assai stone before (Fig. 2a), after carbonization (Fig. 2b), and activated with $CO_2$ (Fig. 2c).

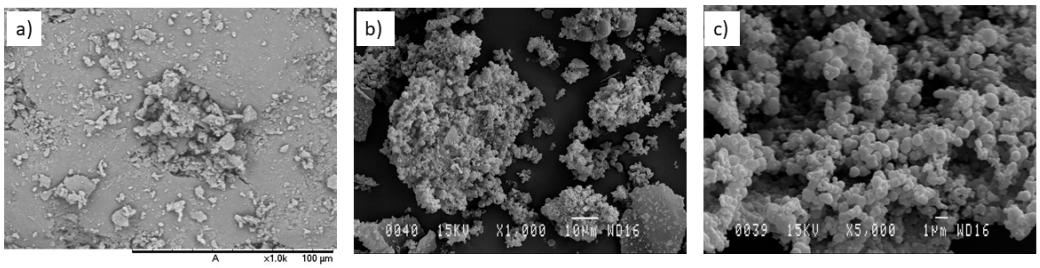


**Fig. 2.** Scanning electron microscopy of a) assai stone (Assai), b) assai stone subjected to microwave-assisted hydrothermal carbonization (Assai MW) and, c) assai stone carbonized and physically activated (Assai MW $CO_2$).

The sample Assai MW exhibits spherical particles with diameters ranging from 1 to 2 μm, typical for the hydrothermal carbonization of α-cellulose [11,19]. These results confirm the effectiveness of the microwave-assisted hydrothermal carbonization process. Moreover, the spherical shape remains after the physical activation process, accompanied with a yield of 35.4%.

*3.3 Textural properties of the porous carbons*

Figure 3a) and b) show the nitrogen adsorption isotherms at -196ºC for samples Assai MW $CO_2$ and Assai CC KOH. The shape of the isotherms is characteristic of Type I, according to the International Union of Pure and applied Chemistry (IUPAC) classification [20]. There is an abrupt increase in the nitrogen uptake at low relative pressure until a plateau is reached. The nitrogen uptake at low relative pressure ($P/P_0<0.1$) is associated to micropores filling (pores below 2 nm), while the presence of the plateau indicates the absence of mesopores (pores above 2 nm).

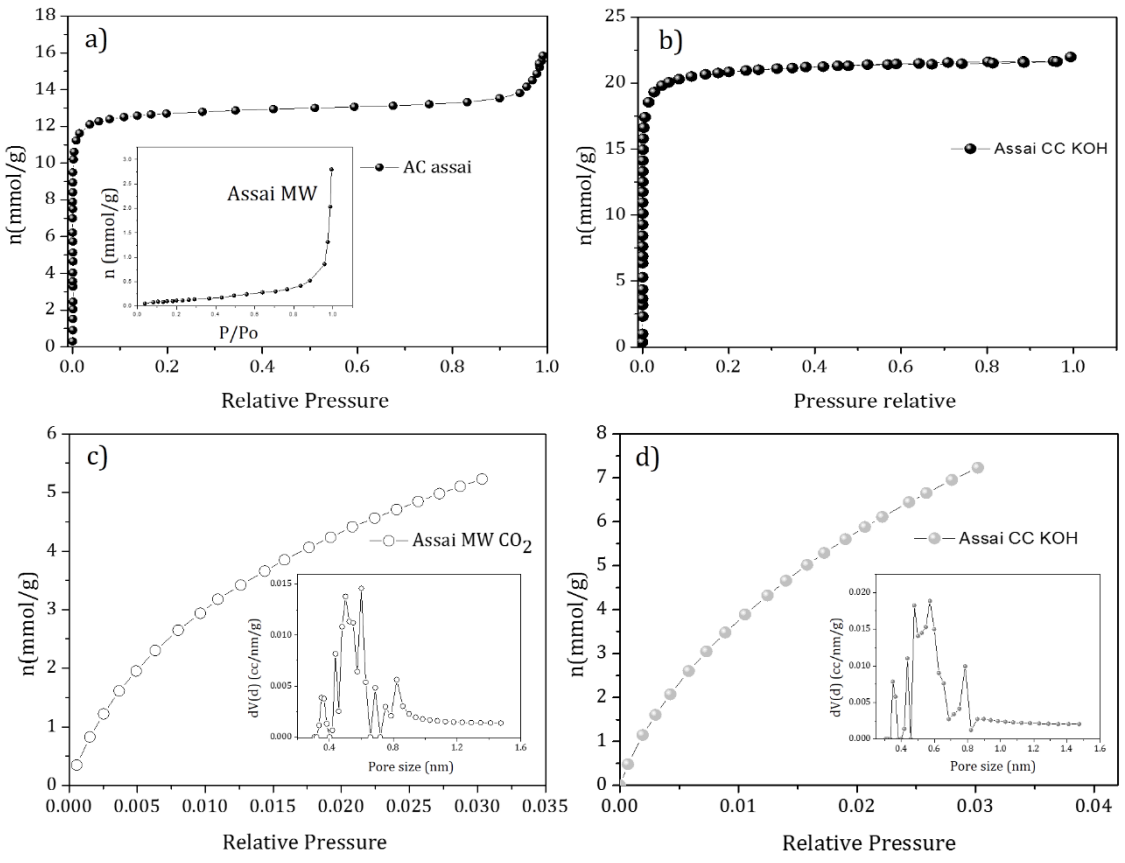


**Fig. 3.** a) $N_2$ isotherms of microwave hydrothermal carbonization and activated carbon derived from assai microwave hydrothermal carbonization. b) $N_2$ adsorption isotherm at 196 ºC of assai chemical activated carbon. c) Adsorption at 0 ºC of $CO_2$ on Assai MW $CO_2$ and pore size distribution. d) Adsorption at 0 ºC of $CO_2$ on assai CC KOH and pore size distribution.

To know more about the microporosity, $CO_2$ adsorption isotherms performed at 0 ºC as shown in Figure 3c) and d), where the inset graphs show the pore size distribution calculated by applying Non-local functional density theory (NLDFT). The results indicate that the mean pores size value is 0.6 nm for sample Assai MW CO2 and around 0.5 nm for sample Assai CC KOH.

Table 2 summarizes the textural properties calculated from the isotherms. Assai MW $CO_2$ exhibits a specific surface area of 1100 $m^2/g$. The similitude of the $N_2$ micropore volume of 0.45 $cm^3/g$ and $CO_2$ micropore volume of 0.47 $cm^3/g$ indicates the evolution of narrow microporosity with narrow pore size distribution in agreement with NLDFT. In the case of conventional carbonization following by chemical activation, the porosity development is higher, with a specific surface area of 1850 $m^2/g$, a $N_2$ pore volume of 0.74 $cm^3/g$ and $CO_2$ pore volume of 0.68 $cm^3/g$.

Table 2. Yields and textural features of the ACs obtained through different routes.

| **Sample** | **Carbonization (Yield %)** | **Activation (Yield %)** | **$S_{BET}$ ($m^2/g$)** | **$V_{N2}$ ($cm^3/g$)** | **$V_{CO2}$ ($cm^3/g$)** |
|---|---|---|---|---|---|
| Assai MW $CO_2$ | 63.5 | 35.4 | 1100 | 0.45 | 0.47 |
| Assai CC $CO_2$ | 24 | 0* | --- | --- | --- |
| Assai CC KOH | 24 | 42 | 1850 | 0.74 | 0.68 |

*AC Assai CC $CO_2$: physical activation after the conventional carbonization completely oxidized the sample.

In principle, both samples are promising for methane storage applications; however, there are other aspects to take into account when scaling-up is considered. On one side, conventional carbonization has a low yield. On the other hand, using KOH as activating agent make difficult the processing at large scale since this chemical is highly corrosive. The MAHC following by $CO_2$ activation is an alternative green-route that can circumvent both drawbacks, resulting in an excellent combination of yield, microporosity evolution,

together with a zero-waste production. Therefore, in the following section the performance of the sample Assai MW $CO_2$ as a methane adsorbent will be evaluated.

*3.4 Methane storage*

Methane adsorption isotherm at high pressure and ambient temperature was measured for sample Assai MW $CO_2$, as shown in Figure 4a). Methane uptake increases with the pressure, first abruptly and then, slowly up to a maximal uptake of approximately 8 wt.% at 4 MPa. This behavior is the expected since the sample contains micropores of around 6 nm. The adsorption potential exerted by micropores of pore size equivalent to one or two-fold the size of methane molecules is extremely high [21]. This indicates that moderate pressures (around 4 MPa in this case) is more than enough to saturate the porosity of the carbon, which is a reasonably adequate pressure for transport and application at large scale.

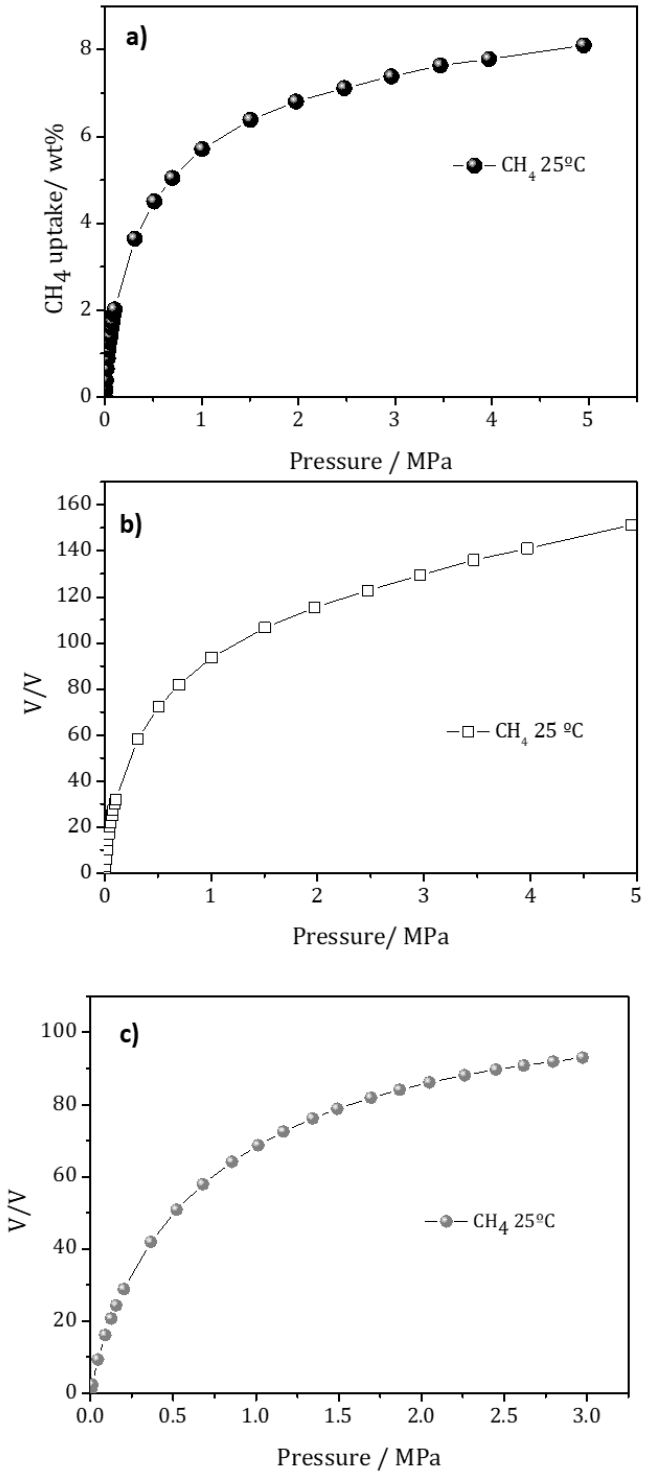


**Fig. 4.** a) $CH_4$ isotherms at 25ºC and up to 4 MPa on gravimetric basis, b) volumetric basis for activated carbon of assai MHTC and c) volumetric basis for activated carbon of assai CC KOH.

Apart from the working pressure, it is also very important to calculate the density of the material since the maximal volume of methane gas must be stored in a minimal volume of solid. Choosing the appropriate density measurement method is a crucial factor when volumetric capacity is evaluated (Wegrzyn and Gurevich 1996). The packing density calculated by compressing the powder is a useful tool because it represents the bulk density. For Assai MW $CO_2$ the bulk density is 0.89 $cm^3/g$ determined by pressing a given mass of activated carbon in a mold with a cross-sectional area of 1.30 $cm^2$ at a pressure of 500 kg/cm. By combining the gravimetric adsorption capacity and the packing density of the activated carbon, it is possible to estimate the volumetric adsorption capacity (V/V) (Figure 4b). At 4 MPa this value is as high as 140 V/V. For assai CC KOH the bulk density is 0.64 $cm^3/g$ and volumetric adsorption capacity at 3 MPa is 93 V/V. Although this value is below the DOE recommended adsorption capacity, it is still very promising to be used in ANG technology considering the green-production methodology and the renewable nature of the carbon precursor.

## 4. Conclusions

The use of biomass to produce microporous carbon seems to be very promising from the processing point of view. Microwave-assisted hydrothermal carbonization (MAHC) is a low-energy alternative method that allows increment the product yield with minimal waste. $CO_2$ activation demonstrated to be suitable to develop narrow porosity without affecting overmuch the spherical morphology. Overall, the biomass-derived renewable microporous carbon shows good bulk density associated with a satisfactory methane storage capacity of 140 V/V.

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**Highlights**

- We used assai stone as raw material to produce microporous carbon for $CH_4$ storage
- MAHC process is a low-energy alternative method that increased carbon yield
- Biomass-derived microporous carbon exhibited a methane storage capacity of 140 V/V